Mercury Speciation in Patrick Bayou

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Mercury Partitioning

- Purpose:
  - Provide a brief summary of the methods used to estimate the proportion of methylmercury in bulk sediment
- Partitioning theory based on:
  - Concentration of MeHg in sediment and porewater
  - Ratio of total organic carbon to dissolved organic carbon

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- Methyl mercury is an organomettalic cation:

$$CH_3Hg^+$$

- Methylmercury is typically associated with:
  - sediment organic matter (SOM)
  - dissolved organic matter (DOM)
- Partitioning in solid phase and porewater can be described as:

$$(SOM)H + CH_3Hg^+ \leftrightarrow (SOM)CH_3Hg + H^+$$

$$(DOM)H + CH_3Hg^+ \leftrightarrow (DOM)CH_3Hg + H^+$$

- It is generally accepted that ratios of SOM to TOC and DOM to DOC are equivalent:

$$SOM:TOC \cong DOM:DOC$$

- Thus, we can substitute TOC and DOC into the previous equilibrium partitioning equations

$$(TOC)H + CH_3Hg^+ \leftrightarrow (TOC)CH_3Hg + H^+$$

$$(DOC)H + CH_3Hg^+ \leftrightarrow (DOC)CH_3Hg + H^+$$

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- Equilibrium constants (K) are equivalent for both equations:

$$A + B \leftrightarrow C + D$$

$$K = \frac{[C][D]}{[A][B]} = 10^{6.5}$$

- Therefore:

$$\frac{[(TOC)CH_3Hg][H^+]}{[(TOC)H][CH_3Hg^+]} = \frac{[(DOC)CH_3Hg][H^+]}{[(DOC)H][CH_3Hg^+]}$$

- Rearranging and canceling like terms:

$$(TOC)CH_3Hg = (DOC)CH_3Hg \times \frac{(TOC)H}{(DOC)H}$$

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- We have site-specific, empirical data for TOC, DOC, and $MeHg_{PW}$
  - $MeHg_{SD}$ can be calculated using this data and previous equation
- Data was collected at 11 stations within the Site
  - Pore water mercury data and DOC were collected from 0-20 cm in 2 cm intervals
    - First five intervals (0-10 cm) was averaged for each location
  - Bulk sediment TOC was analyzed from 0-11 cm from nearest surface grab

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Location	$MeHg_{pw}$ (ng/L)		DOC_{pw} (ug/L)	TOC_{sd} (%)	$MeHg_{sed}$ (ng/kg)	
	Average	Standard Deviation			Average	Standard Deviation
PB-006A	2.47	1.48	20,000	1.48	1,828	1,095
PB-006B	4.7	1.68	19,000	1.48	3,661	1,309
PB-023	1.27	0.73	22,000	0.64	369	212
PB-024	3.46	1.62	24,000	0.92	1,326	621
PB-036	9.51	5.31	42,000	4.36	9,872	5,512
PB-044	0.99	0.42	12,000	1.26	1,040	441
PB-046	3.28	2.35	26,000	1.81	2,283	1,636
PB-052	0.32	0.27	26,000	5.12	630	532
PB-053	3.05	1.58	57,000	2.06	1,102	571
PB-059.1	0.23	0.07	50,000	1.09	51	16
PB-059.2	0.23	0.07	50,000	1	46	14

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- Compared $MeHg_{SD}$ estimates to Total Hg (Hg_T) measured in bulk sediments
  - $MeHg_{SD}$ represented a small fraction of Hg_T; less than 0.2% for all sample locations
    - Not unexpected result given the relatively high sediment sulfides (i.e., AVS) observed in sediment
- Assumed an conservative average of 1% of total mercury measured in bulk sediment is in methylated form for wildlife exposure assessment; remaining 99% inorganic mercury

Hg_T = 10 mg/kg

$MeHg_{SD}$ = 1 mg/kg

Inorganic Hg = 9 mg/kg

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References

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